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COMPLEX EFFECT OF ALUMINUM, PHOSPHOR, AND SODIUM OXIDES ON STRUCTURE AND PROPERTIES OF BORON-FREE TITANIUM ENAMELS

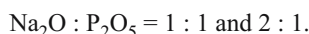
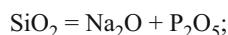
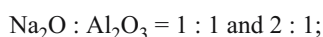
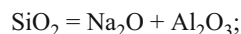
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The effect of complex additives Na₂O, Al₂O₃, and P₂O₅ on the structure and physicochemical properties of boron-free titanium enamels is studied. It is established that introducing Na₂O combined either with Al₂O₃, or with P₂O₅ (optimal ratios of 1 : 1 and from 1 : 1 to 2 : 10, respectively) instead of a part of SiO₂ into a boron-free titanium enamel expands the “list of lattice-forming cations” in glass and increases their fusibility without impairing the whiteness of enamel coatings produced on their basis.

The extensive application of titanium enamels as anti-corrosion and decorative coatings evokes special interest in further research in their structure and properties and their correlation for developing frits with improved parameters.

Lately numerous studies have been carried out for the purpose of lowering or even excluding highly volatile fluorides from boron-bearing enamels. There is also a trend of developing boron-free enamels, primarily caused by the shortage of boron material, and also to its high volatilization in melting enamels and its negative effect on the chemical resistance of enamels. It is also known [1] that even a small excess of alkali oxides in boron-free titanium enamels produces a gray shade in well-opacified vitreous coatings. This is presumably due to the fact that the optical properties of such coatings depend both on the concentration of opacifiers and on the ratio of the oxides perceptibly affecting the structure of enamels [2] and the type of phases crystallizing in firing.

Therefore, the purpose of the present study was to determine the dependence of the physicochemical properties of boron-free titanium enamels on the ratio of its constituent oxides, namely silicon, aluminum, phosphor, and sodium. For this purpose SiO₂ in enamel 1 (Table 1) was replaced in an amount of 2, 4 and 6% (here and elsewhere mol.%, unless otherwise specified) by Na₂O + Al₂O₃ and Na₂O + P₂O₅ in the following ratios:



Experimental enamel glasses were melted in chamotte crucibles in an electric furnace at a temperature of 1260 – 1280°C with subsequent granulation of the melt in water. To produce enamel coatings, the frits were milled adding 7 weight parts of Polozhskoe refractory clay (PLG-2), 0.2 weight parts KCl, and 0.2 weight parts of water. The slip was deposited on steel samples covered by an undercoat and, after drying, fired in a muffle furnace in the temperature interval of 810 – 870°C for 4 min.

We analyzed the properties of synthesized glasses that point to structural modifications in glasses and in glass-based coatings. It was found, for instance, that when SiO₂ is replaced by 2% Na₂O + Al₂O₃, the leachability of frits grows (Fig. 1) from 0.0550 to 0.1192 cm³/g (NaO : Al₂O₃ = 1 : 1)

TABLE 1

Enamel	Replacing SiO ₂	Weight content, %						
		SiO ₂	Na ₂ O	TiO ₂	Na ₃ AlF ₆	Al ₂ O ₃	P ₂ O ₅	MgO
1*	—	57.42	12.35	14.35	9.57	2.87	1.44	2.00
2	Na ₂ O + Al ₂ O ₃	55.42	13.49	14.29	9.53	3.84	1.43	1.99
3		55.30	13.17	14.26	9.51	4.34	1.43	1.99
4		53.42	14.64	14.22	9.49	4.82	1.43	1.98
5		53.21	13.98	14.17	9.45	5.80	1.42	1.97
6		51.44	15.77	14.16	9.44	5.79	1.42	1.97
7		51.26	14.82	14.11	9.41	7.02	1.42	1.97
8	Na ₂ O + P ₂ O ₅	55.20	13.44	14.23	9.49	2.85	2.81	1.98
9		54.98	13.09	14.18	9.45	2.84	3.49	1.98
10		53.00	14.53	14.11	9.41	2.82	4.15	1.97
11		52.60	13.82	14.01	9.34	2.80	5.49	1.95
12		50.85	15.59	14.00	9.33	2.80	5.48	1.95
13		50.27	14.53	13.84	9.23	2.77	7.43	1.93

* Initial enamel.

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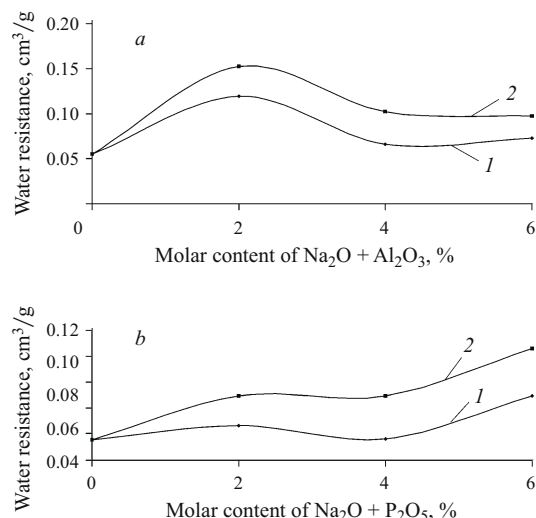


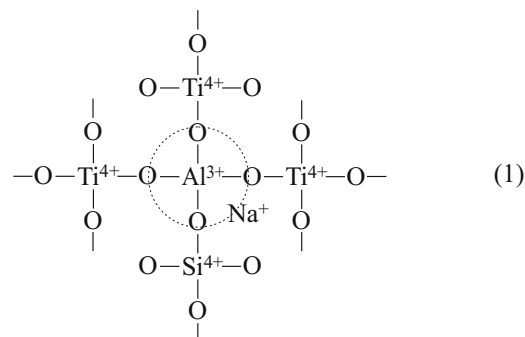
Fig. 1. Water resistance of frits in replacing SiO_2 by $\text{Na}_2\text{O} + \text{Al}_2\text{O}_3$ (a) and $\text{Na}_2\text{O} + \text{P}_2\text{O}_5$ (b) with $\text{Na}_2\text{O} : \text{Al}_2\text{O}_3$ (P_2O_5) ratio equal to 1 : 1 (1) and 2 : 1 (2).

and to $0.1525 \text{ cm}^3/\text{g}$ ($\text{Na}_2\text{O} : \text{Al}_2\text{O}_3 = 2 : 1$), which is due to the strength of the $\text{Ti}-\text{O}-\text{Na}$ bond in titanate groups decreasing after the aluminum ion incorporates into their structure. A further substitution of $\text{Na}_2\text{O} + \text{Al}_2\text{O}_3$ for SiO_2 in the amount of 4 and 6% slightly decreases leachability to $0.0725 \text{ cm}^3/\text{g}$ ($\text{Na}_2\text{O} : \text{Al}_2\text{O}_3 = 1 : 1$) and to $0.0975 \text{ cm}^3/\text{g}$ ($\text{Na}_2\text{O} : \text{Al}_2\text{O}_3 = 2 : 1$), which is possibly related to the incorporation of aluminum tetrahedrons into the silicate glass lattice, considering that aluminum has a larger cation radius than silicon (0.057 against 0.039 nm) and delays the diffusion of alkali ions in glass.

It is interesting that introducing $\text{Na}_2\text{O} + \text{Al}_2\text{O}_3$ in the ratio 1 : 1 to replace 6% SiO_2 decreases the fusion temperature

of enamel coating 7 to 810°C while retaining its high whiteness equal to 81.95% (Table 2). This may be attributed to the fact that the aluminum ion in coordination 4 makes part of the glass structure the lattice-forming agent, which is ensured by the additional introduction of the modifying sodium ion. However, as the strength of the $\text{Al}-\text{O}$ bond (379 kJ/mole) is perceptibly lower than that of the $\text{Si}-\text{O}$ bond (443 kJ/mole), the structural glass lattice becomes less rigid and, accordingly, more fusible, which agrees with the data in [3] reporting an abrupt decrease in the liquidus temperature in the $\text{SiO}_2-\text{Al}_2\text{O}_3-\text{RO}(\text{R}_2\text{O})$ systems along the line with the ratio $\text{Al}_2\text{O}_3 : \text{RO}(\text{R}_2\text{O}) = 1$. This phenomenon is also corroborated by the spectroscopic analysis of glasses (Fig. 2) indicating the shift of the main absorption band at 1030 cm^{-1} to a lower-frequency range, up to 1015 cm^{-1} (enamel 6) and to 985 cm^{-1} (enamel 7), which, in turn, points to the polymerization of the silicon-oxygen skeleton in experimental glasses.

The decrease in the luster of enamel coating 3 to 44% (Table 2) upon the additional introduction of 1% Na_2O and 1% Al_2O_3 can be attributed to the formation of an aluminotitanium silicate structural group, since it may facilitate the growth of the size of titanium dioxide crystals:



The incorporation of aluminum tetrahedrons in the silicate skeleton of the considered glass, as the weight content of Al_2O_3 grows above 4.82%, leads to the situation where an aluminum ion is bonded via oxygen only to two and not to three titanium ions; consequently, the size of the aluminotitanate groups decreases, which contributes to fine-grained crystallization in glass coating 7 and raises its luster to 58% (Table 2). The luster in coating 2 upon introducing 2% $\text{Na}_2\text{O} + \text{Al}_2\text{O}_3$ (their ratio is 2 : 1) decreases less intensely (from 75 to 54%). This is presumably related to the fact that in the formation of clusters (1) an improvement in the crystallization capacity of coatings is opposed by the increased solubility of titanium dioxide when alkali oxides are introduced in excess with respect to aluminum oxide. These alkali oxides are responsible for crystallization of alkali titanates in coatings (Fig. 3, x-ray pattern 6), which decreases their whiteness to 76%.

The introduction of $\text{Na}_2\text{O} + \text{P}_2\text{O}_5$ instead of SiO_2 in the initial enamel frit leads to continuous increase of frit leachability (Fig. 1b), both with the ratio $\text{Na}_2\text{O} : \text{P}_2\text{O}_5$ equal to 1 : 1 (from 0.0550 to $0.0892 \text{ cm}^3/\text{g}$) and the ratio equal to

TABLE 2

Enamel	Quantity of re-placed SiO_2 , %*	Ratio of introduced oxides	Luster, %, at temperature, $^\circ\text{C}$			Whiteness, %, at temperature, $^\circ\text{C}$		
			810	840	870	810	840	870
1	—	—	38	75	67	75.88	81.80	82.86
$\text{Na}_2\text{O} + \text{Al}_2\text{O}_3$								
2	2	2	25	54	62	72.76	76.33	78.30
3	2	1	11	44	55	75.01	81.11	83.15
4	4	2	22	53	66	76.48	79.52	80.98
5	4	1	40	54	64	77.01	81.15	84.81
6	6	2	33	58	64	74.46	76.40	76.67
7	6	1	61	58	59	81.95	83.85	85.51
$\text{Na}_2\text{O} + \text{P}_2\text{O}_5$								
8	2	2	54	64	69	79.54	80.46	80.86
9	2	1	63	64	70	80.61	81.68	82.28
10	4	2	49	70	58	77.81	80.95	82.03
11	4	1	61	72	66	77.85	80.53	80.62
12	6	2	42	43	51	78.00	78.93	80.50
13	6	1	27	69	69	77.63	80.16	81.97

* Molar content.

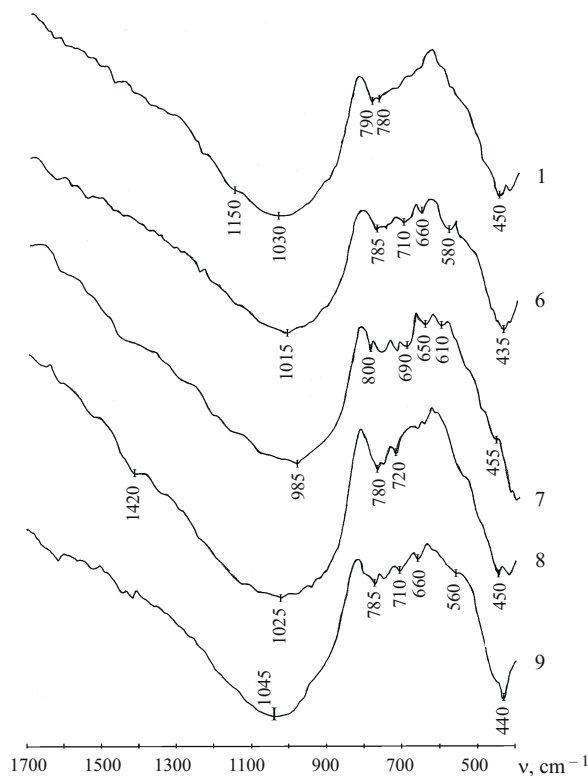
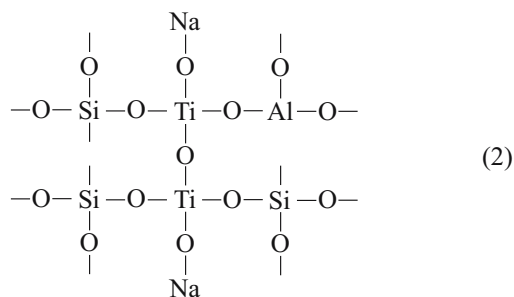


Fig. 2. IR absorption spectra of considered glasses (Spekord-M75). Curve numbers correspond to numbers of enamels.

2 : 1 (to 0.1258 cm³/g). This is primarily caused by the increased quantity of easily leachable sodium oxide. As soon as P₂O₅ is added (1%) instead of SiO₂, the coating luster decreases to 64% (Table 2), which can be presumably interpreted as an increased share of five-coordination titanium ion and, accordingly, the share of groups (2) intensifying the crystallization capacity of coatings [4]:



A further increase in the quantity of P₂O₅ (up to 3%), considering that the P–O bond (464 kJ/mole) is stronger than the Si–O bond (443 kJ/mole), increases the glass viscosity and delays crystal growth, thus providing a close-grained coating structure with whiteness 80% and luster 69% (Table 2). The strengthening of the structural glass lattice on intruding phosphor anhydride is confirmed by IR spectroscopy, indicating the shift of the absorption band responsible for the stretching vibrations of silicon-oxygen groups to higher frequencies: from 1030 to 1045 cm^{−1} (enamel 9).

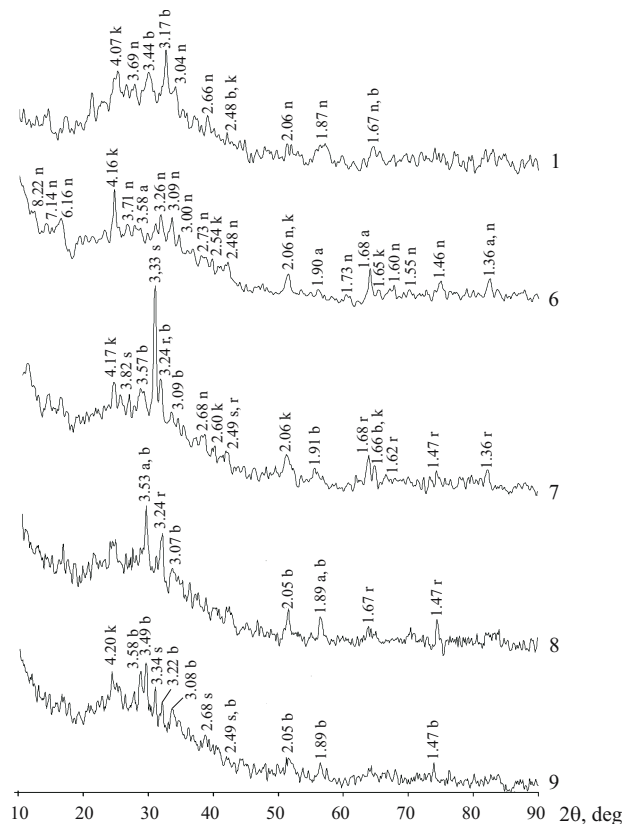


Fig. 3. X-ray patterns of enamel coatings: r) rutile (TiO₂); b) brookite (TiO₂); n) Na₂O · 6TiO₂; k) β-cristobalite; a) anatase (TiO₂); s) Na₂Si₂O₅; curve numbers correspond to numbers of enamels.

The analysis of the crystal phases (Fig. 3) formed after the enamel coatings were fired at 840°C indicates that even introducing excessive sodium oxide together with phosphor oxide does not cause the formation of alkali titanates which (Table 2, enamels 2, 4, and 6 with a decrease P₂O₃ content) lower whiteness to 76%. This may be interpreted by the fact that alkali oxides introduced in a titanium enamel together with phosphor oxide are primarily spent on breaking the double bond P = O of the phosphor cation with oxygen, which is corroborated by the absence of the absorption band (1420 cm^{−1}) typical of this bond in the IR spectrum of glass 9, whereas it is registered in glass 8 with a deficit of alkali oxides.

Based on the obtained results, the following conclusions can be drawn:

- in the case of an equimolar replacement of the lattice-forming component SiO₂ by Na₂O + Al₂O₃ in the ratio 1 : 1, the whiteness of enamel coatings varies insignificantly and is within 81 – 83%, as a result of the localization of the alkali cation on the aluminum tetrahedron, when the latter is incorporated into the structural lattice as a lattice-forming element;
- unlike aluminum oxide, phosphor anhydride can bind 2 moles of the alkali oxide due to breaking the double bond P = O, which is indirectly corroborated by the fact that

enamel coatings retain their whiteness of 80 – 81% within the total concentration range considered;

– the efficiency of a combined introduction of Al_2O_3 and P_2O_5 together with Na_2O (improving the properties of enamel coating) is significantly higher than their separate introduction instead of SiO_2 [1];

– despite the equal quantity of alkali oxides in different glass compositions, they take different positions in the structural glass lattice; alkali ions in enamels with an increased content of aluminum and phosphor oxides are firmly fixed to their polyhedrons, have no negative effect on the solubility of titanium dioxide, and do not contribute to the formation of alkali titanates.

Thus, when alkali oxides are introduced in boron-free titanium-bearing enamel coatings, their whiteness can be preserved only by the simultaneous additional introduction of aluminum and phosphor oxides, so that the quantity of the additionally introduced alkali is equal to the quantity of aluminum oxide added (enamels 3, 5, 7) or is not more than double the quantity of additionally introduced P_2O_5 . When

the considered oxides are added in the specified ratios, the infusibility of coatings does not increase despite the introduction of a substantial quantity of high-melting aluminum oxide, since in this case the structural lattice of glass depolymerizes due to the expanded list of its lattice-forming cations.

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